An efficient synthesis of an optically active (-)-(3*R*, 4*R*, 5*R*)-4-(1-hydroxyl-isopropyl)-3-acetyloxyl-butyrolactone

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An optically active β-hydroxyl–γ-butyrolactone was synthesised from nonchiral starting material by employing reductive cleavage reaction, Sharpless asymmetric epoxidation and dihydroxylation as key steps. This strategy can be used to prepare many chiral β-hydroxyl–γ-butyrolactone analogues. The crystal structure of **10** was determined by X-ray crystallographs.

Keywords: asymmetric synthesis, optically active β-hydroxy butyrolactones, *tuxpanolide*, sharpless asymmetric dihydroxylation, X-ray crystal structure

Recently, the asymmetric synthesis of chiral β-hydroxy-γ-butyrolactones has been a target because they are present in many natural products having antitumor, fungicidal, anti-inflammatory activity.[1,2,3,4] We prepared an optically active β-hydroxyl-γ-butyrolactone as an intermediate for the total synthesis of the natural product Tuxpanolide and its analogues.[5,6] We present here a practical strategy for constructing chiral β-hydroxy-γ-butyrolactones from a cheap nonchiral starting material.

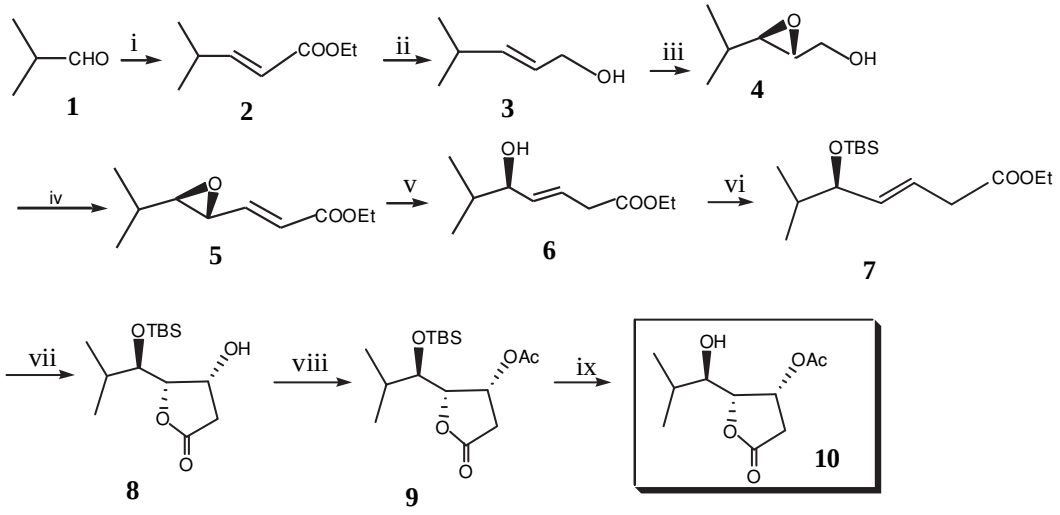
Results and discussion

The synthetic route shown in Scheme 1 led efficiently to compound **10**. The starting material isobutyraldehyde **1** was subjected to the Wittig reaction followed by reduction with $LiAlH_4$–$AlCl_3$ in dry ether to give the allylic alcohol **3**. Sharpless asymmetric epoxidation[7] of the allyl alcohol **3** with (–)-DET, Ti (i-OPr)$_4$, TBHP led to the epoxy alcohol (–)-**4** in 71% yield [8] and 92%ee as determined by ^{1}H NMR analysis of the corresponding Mosher's ester.[9] A coupling reaction of aldehyde obtained by Swern oxidation of **4** and triphenyphosphorane afforded (–)-**5** (41% for two steps). By simply applying the reductive cleavage reaction of α, β-unsaturated ester **5** by magnesium in methanol,[10] we obtained the sole product (–)-**6** in 72% yield. The secondary hydroxyl group of **6** was protected by the TBDMSCl- DMAP–Et_3N system in DMF to produce **7** in 80% yield.

Subsequently Sharpless asymmetric dihydroxylation (ADs) of the key intermediate **7** provided the lactonised dihydroxylation products **8** in 51% yield. (in accordance with the literature precedent[11]) Remarkably, if **7** was protected with an acetyl group, the AD reaction did not happen. Compound **8** obtained was acetylated to give the **9** in 85% yield, followed by the deprotection in the presence of $BF_3{\cdot}Et_2O$ in the dry acetonitrile to give an optically active (–)-(3*R*, 4*S*, 5*R*)-4-(1-hydroxyl-isopropyl)-3-acetyloxyl-butyrolactone **10** in 71% yield**,** $[\alpha]_D^{20}$ –12° (*c*1.0 CH_2Cl_2). The 80%ee of compound **10** was determined by ^{1}H NMR analysis of the corresponding Mosher's ester.[9]

Sharpless asymmetric dihydroxylation (ADs) of olefin and Sharpless asymmetric epoxidation are the indispensable tools for contemporary asymmetric organic synthesis. They provided good selectivity for the constructions of three chiral carbons in the molecular of compound **10**. Further, the structural confirmation of compound **10** was performed on the basis of single crystal X-ray diffraction. It showed the absolute configuration as 3R, 4R, 5R (Fig. 1).

A hydrogen bond was found between the H-5 atom on O-5 and the O-1 atom and between C-1 and C-4. d(D-H) is 0.88 Å, d(H..A) is 2.00 Å, d(D.. A) is 2.87 Å, <DHA is 170°. This hydrogen bond was not very strong; accounting for the poor crystallinity.



Scheme 1 (i) Ph_3P=CHCOOEt, CH_2Cl_2, 0 °C r.t.; (ii) $LiAlH_4$:$AlCl_3$ 1:0.3, Et_2O, –78 °C; (iii) Ti(O-*i*–Pr)$_4$, (–)-DET, TBHP, CH_2Cl_2, –20 °C; (iv) (a) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, –78 °C; (b) Ph_3P=CHCOOEt, CH_2Cl_2, r.t.; (v) Mg, MeOH, –23 °C. (vi) TBDM Cl, Et_3N, DMAP, DMF, r.t; (vii) AD-mix-α, $CH_3SO_2NH_2$, *t*-BuOH-H_2O, r.t.(viii) Ac_2O, DMAP, Py, r.t.; (xi) $BF_3{\cdot}Et_2O$, CH_3CN, 0°C.

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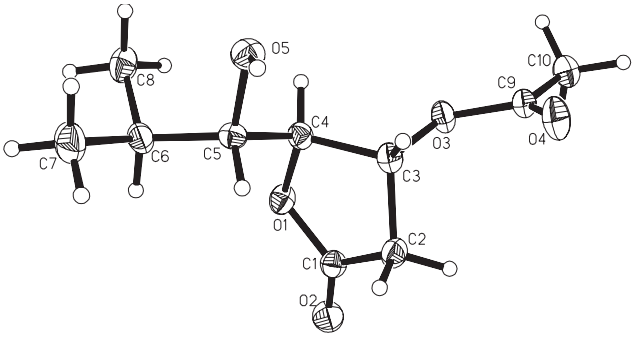

Fig. 1 X-ray molecular structure of compound 10.

In conclusion, we successfully accomplished the asymmetric synthesis of an optically active β-hydroxyl-γ- butyrolactone **10** through nine steps. According to the above strategy, the stereochemistry at C-3, C-4, C-5 of its analogues can be efficiently controlled. This work is significant in the asymmetric total synthesis of the natural products bearing the optically active β-hydroxyl-γ-butyrolactone unit from an achiral material.

Experimental

General methods

IR spectra were recorded on an FT-170SX spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AM-200 or AM-400 MHz instruments using tetramethylsilane (TMS) as the internal standard. Mass spectra were recorded on VG ZAB-HS or VG-7070 (70 ev) spectrameters. GLC analyses were carried out on a Shimadzu GC-9AM instrument. Optical rotations were measured with a Perkin Elmer 341 instrument. Melting points was determined by MEL-TEMP II and are uncorrected. X-ray crystallographic data were collected at room temperature on a Rigaku AFC7R diffractometer.

Crystal data

Compound **10** was formed after recrystallisation in EtOAc. The crystal structure was solved by direct methods and refined using Fourier techniques. Relevant numerical data are given in Table 1, atomic coordinates and B_{iso}/B_{eq} are listed in Table 2. Bond Angles for compound **10** was shown in Table 3.

(–)-(4R,5R)-6-methyl-4,5-epoxy-2-heptenoate (**5**): To a stirred solution of oxalyl chloride (0.23 ml, 2.6 mmol) in CH_2Cl_2 (10ml) at –78 °C was added dropwise DMSO (0.37 ml, 5.2 mmol). Upon complete addition, **4** (150 mg, 1.3 mmol) dissolved in CH_2Cl_2 (0.5 ml) was added dropwise. The initially clear solution became white and cloudy after stirring for 1.5 h. Triethylamine (657 mg, 6.5 mmol) was then added dropwise at –78 °C. Then the reaction mixture was warmed slowly to –10 °C for 2 h and quenched by the addition of water (0.3 ml). The organic layer was separated and washed with water and brine; the combined aqueous washes were extracted with CH_2Cl_2. The organic phases were combined and dried over $MgSO_4$. After the removal of solvent, a buff oil (100 mg) was obtained. To a stirred solution of (ethoxycarbonylmethylene) triphenylphosphorane (306 mg, 0.89 mmol) in dry CH_2Cl_2 (10 ml) was added to the above oil (100 mg) under an Ar atmosphere. The reaction mixture was stirred for 2 h at room temperature and the solvent was evaporated. The crude residue was purified by column chromatography (petroleum: EtOAc, 32:1) to furnish **5** as an oil (110 mg, two steps 41%). $[\alpha]_D^{27}$ –10.6° (c 1.4 CH_2Cl_2). IR (film): 2962, 1725, 1661, 1593, 1439, 1307, 1275, 1192, 978, 857 cm^{-1}. ^{1}H NMR (200 M , $CDCl_3$): δ0.96 (d, *J* = 7.1 Hz, 3H), 1.01 (d, *J* = 6.8 Hz, 3H), 1.27 (t, *J* = 7.0Hz, 3H), 1.56–1.64 (m, 1H), 2.65 (dd, *J*=1.8, 6.6 Hz, 1H), 3.23 (dd, *J* = 6.8, 1.9 Hz, 1H), 4.20 (q, *J* = 7.0 Hz, 2H), 6.12 (d, *J* = 15.6 Hz, 1H), 6.69 (dd, *J* = 15.6, 6.7 Hz, 1H). ^{13}C NMR (50 M, $CDCl_3$): δ14.07, 18.06, 18.76, 30.41, 55.19, 60.48, 66.50, 123.26, 144.79, 165.55. EIMS: *m/e* 185, 139, 111, 98, 83, 56, 45, 43, 41. HRMS ($M+NH_4$) calcd for $C_{10}H_{20}O_3N$ 202.2729, found 202.2757.

(–)-(5R)-6-methyl-5-hydroxy-3-heptenoate (**6**): The substrate **5** (160 mg, 0.87 mmol) in dry methanol (5 ml) was cooled at –23 °C before magnesium powder (63 mg, 2.61 mmol) was added. The reaction mixture was stirred for 2 h under Ar atmosphere. To the grey solution was added an equal volume of diethyl ether, the whole mixture was filtered through a silica gel pad and concentrated *in vacuo*. The crude product was purified by flash chromatography (SiO_2) (petroleum:EtOAc, 8:1) to obtain a colourless oil **6** (110 mg, 72%). $[\alpha]_D^{26}$ +12.1° (*c*1.8 CH_2Cl_2). IR (film): 3416, 2922, 1733, 1626, 1405, 1381, 1158, 1072, 1023 cm^{-1}. ^{1}H NMR (200 M, $CDCl_3$): δ 0.87 (d, *J* = 2.4 Hz, 3H), 0.90 (d, *J* = 2.4 Hz, 3H), 1.22 (t, *J* = 7.2 Hz, 3H), 1.63–1.70 (m, 1H), 3.05 (brd, 2H), 3.86 (t, *J* = 6.4 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 5.55 (dd, *J* = 7.2, 15.4 Hz, 1H), 5.73 (dt, *J* = 7.5, 15.4 Hz, 1H). ^{13}C NMR (50 M, $CDCl_3$): δ 14.11, 17.88, 18.10, 33.64, 37.69, 60.66, 72.23, 123.80, 135.30, 171.65. EIMS: *m/e* 143, 130, 97, 73, 43. HRMS ($M+NH_4$) calcd for $C_{10}H_{22}O_3N$ 204.1594, found 204.1597.

(–)-(5R)-6-methyl-5-tert-butyldimethyl-silyloxy-3-heptenoate (**7**): To a solution of **6** (350 mg, 1.88 mmol) in anhydrous DMF (3 ml) at r.t. under Ar atmosphere, were added Et_3N (1.44 ml), TBDMSCl (340 mg, 2.26 mmol) and DMAP (12 mg, 0.094 mmol). The mixture was stirred 6 h at r.t., quenched with a saturated solution of NH_4Cl (1.5 ml) and diluted with Et_2O. The organic layer was washed with H_2O and brine, dried over $MgSO_4$ and concentrated to give the crude product which was purified by silica gel column chromatography (petroleum:EtOAc,16:1), to yield a colourless oil **10** (463 mg, 82%). $[\alpha]_D^{20}$ –9° (*c* 1.0 CH_2Cl_2). IR (film): 2920, 1733, 1626, 1405, 1381, 1158, 1072, 1023 cm^{-1}. ^{1}H NMR (200 M, $CDCl_3$): δ0.04 (s, 3H), 0.08 (s, 3H), 0.83 (brs, 3H), 0.86 (brs, 3H), 0.90 (s,12H), 1.22 (t, *J* = 7.2 Hz, 3H), 1.63–1.70 (m, 1H), 3.04–3.09 (m, 2H), 3.82 (t, *J* = 6.4 Hz, 1H), 4.18 (q, *J*= 7.2 Hz, 2H), 5.56–5.64 (m, 2H). EIMS: *m/e* 243, 213, 185, 143, 130, 117, 97, 73, 43. HRMS ($M+NH_4$) calcd for $C_{16}H_{36}O_3NSi$ 318.2463, found 318.3009.

(–)-(3R,4S,5R)-4-(1-tert-butyldimethylsiloxy-isopropyl)-3-hydroxy-butyrolactone (**8**): To compound **7** (208 mg, 0.68 mmol) was added a mixture of *t*-BuOH (3.5 ml), H_2O (3.5 ml), AD-mix α (960 mg, 0.69 mmol), and methanesulfonyl amide (70 mg, 0.69 mmol). The solution was stirred for 72 h at 0 °C. After the addition of saturated Na_2SO_3 (1.0 g, 0.69 mmol), the mixture was stirred for 40 minutes and diluted with EtOAc. The organic layer was washed with H_2O and brine, dried over $MgSO_4$ and concentrated to give the crude product which was purified by silica gel column chromatography (petroleum: EtOAc, 4:1), to yield a colourless fissile crystal **11** (82 mg, 45%). $[\alpha]_D^{20}$ –10.0° (*c* 1.0 CH_2Cl_2). IR (film):3467, 2956, 2930, 2856, 1770, 1754, 1469, 1389, 1252, 1128, 1065, 841 cm^{-1} ^{1}H NMR (400 M, $CDCl_3$): δ 0.14 (s, 3H), 0.20 (s, 3H), 0.91(s, 12H), 1.04 (d, *J* = 4.2 Hz, 3H), 1.06 (d, *J* = 4.2 Hz, 3H), 2.03–2.08(m, 1H), 2.60(brd, 1H), 2.69 (dd, *J* =4 .8, 17.4 Hz, 1H), 4.08 (dd, *J* = 1.9, 7.0 Hz, 1H), 4.33–4.35 (m, 1H), 4.73 (dd, *J* = 1.8, 7.7 Hz, 1H), 4.96 (d, *J* = 3.2 Hz, OH). ^{13}C NMR (100 M, $CDCl_3$): δ 18.10, 19.02, 19.21, 25.82, 31.48, 40.48, 69.89, 81.38, 175.36. EIMS: *m/e* 287, 245, 231, 201, 187, 171, 159, 147, 129, 117, 113, 101, 25, 43. HRMS ($M+NH_4$) calcd for $C_{14}H_{32}O_4NSi$ 306.2095, found 306.2099

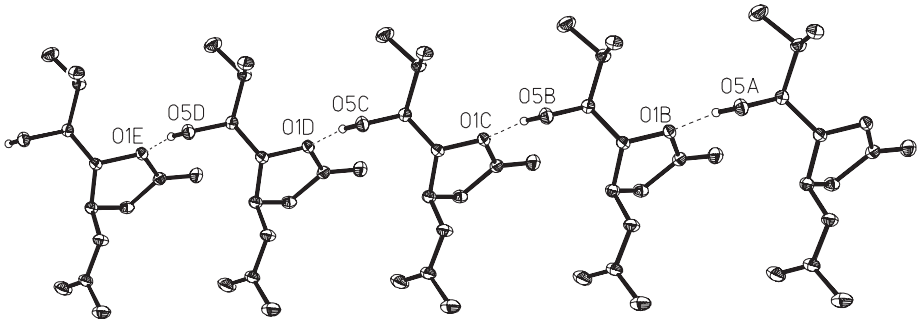

Fig. 2 Hydrogen bond of compound 10.

Table 1 Crystal data and structure refinement for compound **10**

Empirical formula	$C_{10}H_{16}O_5$
Formula weight	216.23
Temperature	291(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	*a* = 10.354(2) A α = 90°
	b = 5.5668(11) A β = 113.79(3)°
	c = 10.558(2) A γ = 90°
Volume	556.86(19) A^3
Z, Calculated density	2, 1.290 mg/m^3
Absorption coefficient	0.103 mm^{-1}
F(000)	232
Crystal size	0.20 × 0.18 × 0.18 mm
Refinement method	
Full-matrix least-squares on F^2	
Data / restraints / parameters	2051 / 1 / 141
Goodness-of-fit on F^2	1.027
Final R indices [$I>2\sigma(I)$]	R1 = 0.0409, wR2 = 0.0977
R indices (all data)	R1 = 0.0526, wR2 = 0.1023
Absolute structure parameter	2.2(13)

Table 2 Atomic coordinates (× 10^{-4}) and equivalent isotropicdisplacement parameters ($A^{-2} \times 10^{-3}$) for P21

	X	*Y*	*Z*	*U*(eq)
O(1)	205(2)	2914(2)	2818(2)	42(1)
O(2)	1006(2)	1141(3)	4889(2)	57(1)
O(3)	2979(2)	4678(3)	2866(2)	46(1)
O(4)	4564(2)	7550(4)	3913(2)	68(1)
O(5)	-412(2)	8729(3)	1086(2)	48(1)
C(1)	1065(2)	2816(4)	4194(2)	41(1)
C(2)	2001(2)	4974(4)	4588(2)	44(1)
C(3)	1935(2)	5917(4)	3218(2)	40(1)
C(4)	491(2)	5069(4)	2179(2)	37(1)
C(5)	-666(2)	6933(4)	1925(2)	36(1)
C(6)	-2173(2)	5975(4)	1215(2)	45(1)
C(7)	-3215(3)	7993(6)	1091(3)	67(1)
C(8)	-2477(2)	4847(5)	-189(3)	55(1)
C(9)	4286(2)	5642(4)	3323(2)	45(1)
C(10)	5266(3)	4074(6)	3002(3)	62(1)

U(eq) is defined as one third of the trace of the orthogonalised Uij tensor.

(–)-(3R,4S, 5R)-4-(1-tert-butyldimethylsilyloxy)isopropyl-3-acetoxy-butyrolactone (**9**): To a solution of **8** (210 mg, 0.72 mmol) in pyridine (2.0ml) was added acid anhydride (88 mg, 0.86 mmol) and DMAP (7 mg, 0.05 mmol). The reaction mixture was stirred for 3 h at room temperature. The mixture was extracted with EtOAc and then the organic layer was washed with aqueous 10% NaOH, 5% HCl, H_2O and brine, respectively, then dried over $MgSO_4$. After removal of the solvent, the residue was subjected to silica gel column chromatography (petroleum:EtOAc, 8:1) to finish **9** (200 mg, 85%) as a pale yellow solid. M.p.: 80–82 °C $[\alpha]_D^{20}$ –11° (*c*1.0 CH_2Cl_2). IR (film): 2956, 2925, 2856,1770,1738, 1469,1373, 1252, 1183 cm^{-1}. ^1H NMR (200 M, $CDCl_3$): δ 0.02 (s, 6H), 0.88 (s, 9H), 2.01 (m, 1H), 2.08 (s, 3H), 2.58 (brd, *J* = 18.2Hz, 1H), 2.84 (dd, *J* = 4.6Hz, 18.2Hz, 1H), 4.05 (m, 1H), 4.30 (dd, *J* = 3.2Hz, 5.9Hz, 1H), 5.29 (m, 1H). EIMS (70 ev) *m/z* 330, 287, 245, 231, 201, 187, 171, 159, 147, 129, 117, 113. HRMS ($M+NH_4$) calcd for $C_{16}H_{34}O_5NSi$ 348.2495, found 348.2396.

(–)-(3R, 4R, 5R)-4-(1-hydroxylisopropyl)-3-acetoxy-butyrolactone (**10**): To a solution of **9** (102 mg, 0.4 mmol) in dry acetonitrile (4.0 ml) was added $BF_3{\cdot}Et_2O$ 110mg (0.8 mmol) at 0°C under Ar atmosphere, after the reaction mixture was stirred for an hour, H_2O was added slowly to quench the mixture. Then the solvent was evaporated and the residue was extracted with EtOAc. The organic layer was washed with aqueous 5% NaOH, H_2O and brine, respectively, then dried over $MgSO_4$. After removal of the solvent, the residue was subjected to silica gel column chromatography to give **2** (55 mg, 70%) as a colourless crystalline solid. M.p.: 87–88 °C. $[\alpha]_D^{20}$ +4° (*c* 1.5 CH_2Cl_2) IR (CH_2Cl_2) ν_{max} 3492, 2965, 2879, 1786, 1743, 1468, 1374, 1241, 1168, 1035, 954, 910 cm^{-1}. ^1H NMR (200M, $CDCl_3$) δ 0.94 (d, *J* = 7.0Hz, 3H), 1.04 (d, *J* = 7.0Hz, 3H), 2.03 (m, 1H), 2.17 (s, 3H), 2.50 (brs, OH), 2.62 (brd, *J* = 18.0Hz, 1H), 2.92 (dd, *J* = 5.4Hz, 18.0Hz, 1H), 3.69(dd, 1H), 4.36 (dd, *J* = 3.4Hz, 9.4Hz, 1H), 5.61 (m, 1H). EIMS (70 ev) *m/z* 217, 199, 187, 113, 84, 43.^{13}C NMR (75Hz, $CDCl_3$): 14.37, 19.34, 20.91, 29.42, 36.80, 70.90, 81.69, 171.05, 174.02. HRMS ($M+NH_4$) calcd for $C_{10}H_{20}O_5N$ 233.9895, found 233.9882.

The X-ray crystal structure was determined by Zhengzhou University X-ray analysis group. We thank the Natural Science Foundation of China (20272020) and Special Research Grant for Doctor Sites in Chinese University.

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Table 3 Bond angles for compound **10**

C1 O1 C4 110.91(16) .	C9 O3 C3 117.50(17) . .	C5 O5 H5E 107(2) . .
O2 C1 O1 120.5(2) .	O2 C1 C2 129.9(2) .	O1 C1 C2 109.59(19) . .
C1 C2 C3 103.82(18) . .	C1 C2 H2A 111.0 . .	C3 C2 Hs 2A 111.0 . .
C1 C2 H2B 111.0 . .	C3 C2 H2B 111.0 . .	H2A C2 H2B 109.0 . .
O3 C3 C2 109.20(18) .	O3 C3 C4 106.47(17) . .	C2 C3 C4 103.42(18) . .
O3 C3 H3A 112.4 . .	C2 C3 H3A 112.4	C4 C3 H3A 112.4 . .
O1 C4 C5 110.38(16) .	O1 C4 C3 104.10(16) . .	C5 C4 C3 112.83(17) . .
O1 C4 H4A 109.8 .	C5 C4 H4A 109.8 .	C3 C4 H4A 109.8 . .
O5 C5 C4 104.90(17) . .	O5 C5 C6 110.29(17) .	C4 C5 C6 115.03(17) . .
O5 C5 H5A 108.8 . .	C4 C5 H5A 108.8 . .	C6 C5 H5A 108.8 . .
C8 C6 C7 111.0(2) . .	C8 C6 C5 112.99(19) .	C7 C6 C5 109.4(2) . .
C8 C6 H6A 107.8 .	C7 C6 H6A 107.8 .	C5 C6 H6A 107.8 .
C6 C7 H7A 109.5	C6 C7 H7B 109.5	H7A C7 H7B 109.5 .
C6 C7 H7C 109.5 . .	H7A C7 H7C 109.5 .	H7B C7 H7C 109.5 . .
C6 C8 H8A 109.5 . .	C6 C8 H8B 109.5 .	H8A C8 H8B 109.5 .
C6 C8 H8C 109.5 . .	H8A C8 H8C 109.5 . .	H8B C8 H8C 109.5 . .
O4 C9 O3 122.0(2) .	O4 C9 C10 126.6(2) . .	O3 C9 C10 111.4(2) .
C9 C10 H10A 109.5 .	C9 C10 H10B 109.5 .	H10A C10 H10B 109.5 .
C9 C10 H10C 109.5 .	H10A C10 H10C 109.5 .	H10B C10 H10C 109.5

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